PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 7 : C08J 9/00

A2

(11) International Publication Number: WO 00/47657

(43) International Publication Date: 17 August 2000 (17.08.00)

(21) International Application Number: PCT/US00/03682

(22) International Filing Date: 11 February 2000 (11.02.00)

(30) Priority Data:
60/119,816 12 February 1999 (12.02.99) US

(71) Applicant (*for all designated States except US*): THE DOW CHEMICAL COMPANY [US/US]; 2030 Dow Center, Midland, MI 48674 (US).

(72) Inventors; and
(75) Inventors/Applicants (*for US only*): FIBIGER, Richard, F. [US/US]; 3870 Johns Lane, Midland, MI 48642 (US). SUH, Kyung, W. [US/US]; 6204 Evergreen Court, Midland, MI 48642 (US). BARGER, Mark, A. [US/US]; 129 Helen Street, Midland, MI 48640 (US). SCHOMAKER, Joseph, A. [US/US]; 2280 South Duncan Road, Midland, MI 48640 (US). LIANG, Wenbin [CN/US]; 6319 Aspen Cove, Sugarland, TX 77479 (US). MACKEY, George, A. [US/US]; 6007 Oak Hollow Court, Midland, MI 48640 (US). TUNG, Harvey, C. [US/US]; 684 Carriage Court, Newark, OH 43055 (US).

(74) Agent: KORFHAGE, Glenn, H.; Intellectual Property, P.O. Box 1967, Midland, MI 48641-1967 (US).

(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published
Without international search report and to be republished upon receipt of that report.

(54) Title: NANOCOMPOSITE ARTICLES AND PROCESS FOR MAKING

(57) Abstract

An improved process for making a structural foamed polymer, a multilayer polymer film, sheet or tube, a pultrusion polymer profile, a compression molded extruded fiber reinforced polymer pre-form, a strand foamed polymer and a SCORIM formed polymer article. The improvement includes the step of dispersing a multi-layered silicate material with the polymer so that the polymer has dispersed therein single layers of silicate material, double layers of silicate material, triple layers of silicate material, four layers of silicate material, five layers of silicate material and more than five layers of silicate material, the volume percent of the one, two, three, four and five layers of silicate material greater than the volume percent of the more then five layers of silicate material. In each of the above embodiments an important benefit of the instant invention is the orientation of the plane of the layers of silicate material. Preferably, most of the layers of silicate material have substantially the same orientation within thirty degrees of angle. Such orientation improves the properties of the product and provides a practical way to make larger products. The amount of multi-layered silicate material used is preferably between one and twenty percent.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania
AM	Armenia
AT	Austria
AU	Australia
AZ	Azerbaijan
BA	Bosnia and Herzegovina
BB	Barbados
BE	Belgium
BF	Burkina Faso
BG	Bulgaria
BJ	Benin
BR	Brazil
BY	Belarus
CA	Canada
CF	Central African Republic
CG	Congo
CH	Switzerland
CI	Côte d'Ivoire
CM	Cameroon
CN	China
CU	Cuba
CZ	Czech Republic
DE	Germany
DK	Denmark
EE	Estonia
ES	Spain
FI	Finland
FR	France
GA	Gabon
GB	United Kingdom
GE	Georgia
GH	Ghana
GN	Guinea
GR	Greece
HU	Hungary
IE	Ireland
IL	Israel
IS	Iceland
IT	Italy
JP	Japan
KE	Kenya
KG	Kyrgyzstan
KP	Democratic People's Republic of Korea
KR	Republic of Korea
KZ	Kazakstan
LC	Saint Lucia
LI	Liechtenstein
LK	Sri Lanka
LR	Liberia
LS	Lesotho
LT	Lithuania
LU	Luxembourg
LV	Latvia
MC	Monaco
MD	Republic of Moldova
MG	Madagascar
MK	The former Yugoslav Republic of Macedonia
ML	Mali
MN	Mongolia
MR	Mauritania
MW	Malawi
MX	Mexico
NE	Niger
NL	Netherlands
NO	Norway
NZ	New Zealand
PL	Poland
PT	Portugal
RO	Romania
RU	Russian Federation
SD	Sudan
SE	Sweden
SG	Singapore
SI	Slovenia
SK	Slovakia
SN	Senegal
SZ	Swaziland
TD	Chad
TG	Togo
TJ	Tajikistan
TM	Turkmenistan
TR	Turkey
TT	Trinidad and Tobago
UA	Ukraine
UG	Uganda
US	United States of America
UZ	Uzbekistan
VN	Viet Nam
YU	Yugoslavia
ZW	Zimbabwe

NANOCOMPOSITE ARTICLES AND PROCESS FOR MAKING

This application is under a United States Government contract with The Department of Commerce (NIST)-Advanced Technology Program Project #70NANB7H3028.

BACKGROUND

This invention relates to polymer systems reinforced with delaminated or exfoliated multi-layered silicates, that is, nanocomposite polymer systems.

Nanocomposite polymers are compositions comprising a relatively high number (but relatively low weight) of exfoliated multi-layered silicate material dispersed in a given volume of continuous polymer matrix, United States Patent 5,717,000 to Seema V. Karande, Chai-Jing Chou, Jitka H. Solc and Kyung W. Suh, herein fully incorporated by reference. As discussed in the '000 patent and as is well known in the art, nanocomposite polymers exhibit many increased physical property enhancements at a much lower volume percent of filler than conventionally filled polymers. For example, when nanocomposite polymers are formed into a film, the exfoliated multi-layered silicate material can be oriented in the direction parallel to the film surface, which contributes to the barrier properties of the film, United States Patent 5,164,460, herein fully incorporated by reference.

SUMMARY OF THE INVENTION

The instant invention has twelve embodiments. The first embodiment is an improved process for making a structural foamed polymer comprising the steps of dispersing a gas-producing material into a fluid polymer at a first pressure followed by a second pressure less than the first pressure, the difference between the first pressure and the second pressure being sufficient to generate bubbles of gas in the fluid polymer. The improvement comprises the step of dispersing a multi-layered silicate material with the polymer so that the polymer has dispersed therein single layers of silicate material, double layers of silicate material, triple layers of silicate material, four layers of silicate material, five layers of silicate material and more than five layers of silicate material, the volume percent of the one, two, three, four and five layers of silicate material being greater than the volume percent of the more than five layers of silicate material.

The second embodiment of the instant invention is an improved structural foamed polymer comprising gas cells having polymer walls. The improvement comprises the polymer having dispersed therein single layers of silicate material, double layers of

silicate material, triple layers of silicate material, four layers of silicate material, five layers of silicate material and more than five layers of silicate material, the volume percent of the one, two, three, four and five layers of silicate material being greater than the volume percent of the more than five layers of silicate material.

The third embodiment of the instant invention is an improved process for making a multilayer polymer film or sheet comprising the step of coextruding layers of at least two different polymers or at least two different layers of the same polymer to form the multilayer polymer film or sheet. The improvement comprises the step of dispersing a multi-layered silicate material with at least one polymer so that the at least one polymer has dispersed therein single layers of silicate material, double layers of silicate material, triple layers of silicate material, four layers of silicate material, five layers of silicate material and more than five layers of silicate material, the volume percent of the one, two, three, four and five layers of silicate material being greater than the volume percent of the more than five layers of silicate material.

The fourth embodiment of the instant invention is an improved multilayer polymer film, sheet or tube comprising layers of at least two different polymers or at least two layers of the same polymer. The improvement comprises at least one polymer having dispersed therein single layers of silicate material, double layers of silicate material, triple layers of silicate material, four layers of silicate material, five layers of silicate material and more than five layers of silicate material, the volume percent of the one, two, three, four and five layers of silicate material being greater than the volume percent of the more than five layers of silicate material.

The fifth embodiment of the instant invention is an improved pultrusion process comprising the steps of impregnating a reinforcing fiber bundle with a polymer and forming a structural profile. The improvement comprises the step of dispersing a multi-layered silicate material with the polymer so that the polymer has dispersed therein single layers of silicate material, double layers of silicate material, triple layers of silicate material, four layers of silicate material, five layers of silicate material and more than five layers of silicate material, the volume percent of the one, two, three, four and five layers of silicate material being greater than the volume percent of the more than five layers of silicate material.

The sixth embodiment of the instant invention is an improved pultrusion structural profile comprising a reinforcing fiber bundle impregnated with a polymer. The

improvement comprises the polymer having dispersed therein single layers of silicate material, double layers of silicate material, triple layers of silicate material, four layers of silicate material, five layers of silicate material and more than five layers of silicate material, the volume percent of the one, two, three, four and five layers of silicate material being greater than the volume percent of the more than five layers of silicate material.

The seventh embodiment of the instant invention is an improved compression molding process comprising the step of compression molding an extruded fiber reinforced polymer pre-form. The improvement comprises the step of dispersing a multi-layered silicate material with the polymer so that the polymer has dispersed therein single layers of silicate material, double layers of silicate material, triple layers of silicate material, four layers of silicate material, five layers of silicate material and more than five layers of silicate material, the volume percent of the one, two, three, four and five layers of silicate material being greater than the volume percent of the more than five layers of silicate material.

The eighth embodiment of the instant invention is an improved article, the article made by compression molding an extruded fiber reinforced polymer pre-form. The improvement comprises the polymer having dispersed therein single layers of silicate material, double layers of silicate material, triple layers of silicate material, four layers of silicate material, five layers of silicate material and more than five layers of silicate material, the volume percent of the one, two, three, four and five layers of silicate material being greater than the volume percent of the more than five layers of silicate material.

The ninth embodiment of the instant invention is an improved process for making strand foamed polymer comprising the steps of extruding a polymer through a plurality of openings to form strands and then coalescing the strands. The improvement comprises the step of dispersing a multi-layered silicate material with the polymer so that the polymer has dispersed therein single layers of silicate material, double layers of silicate material, triple layers of silicate material, four layers of silicate material, five layers of silicate material and more than five layers of silicate material, the volume percent of the one, two, three, four and five layers of silicate material being greater than the volume percent of the more than five layers of silicate material.

The tenth embodiment of the instant invention is improved strand foamed polymer article. The improvement comprises the polymer having dispersed therein single layers of silicate material, double layers of silicate material, triple layers of silicate material, four layers of silicate material, five layers of silicate material and more than five layers of

silicate material, the volume percent of the one, two, three, four and five layers of silicate material being greater than the volume percent of the more than five layers of silicate material.

The eleventh embodiment of the instant invention is an improved SCORIM process for molding a polymer into an article comprising the step of introducing the polymer into a mold by reciprocating flow. The improvement comprises the step of dispersing a multi-layered silicate material with the polymer so that the polymer has dispersed therein single layers of silicate material, double layers of silicate material, triple layers of silicate material, four layers of silicate material, five layers of silicate material and more than five layers of silicate material, the volume percent of the one, two, three, four and five layers of silicate material being greater than the volume percent of the more than five layers of silicate.

The twelfth embodiment of the instant invention is an improved SCORIM molded polymer article. The improvement comprises the polymer having dispersed therein single layers of silicate material, double layers of silicate material, triple layers of silicate material, four layers of silicate material, five layers of silicate material and more than five layers of silicate material, the volume percent of the one, two, three, four and five layers of silicate material being greater than the volume percent of the more than five layers of silicate material.

In each of the above embodiments an important benefit of the instant invention is the orientation of the plane of the layers of silicate material. More specifically, most of the layers of silicate material have substantially the same orientation (within thirty degrees of angle of the major surface of the fabricated material or of the interface of a multilayer structure) and this orientation improves the properties of the product. In the structural foamed polymer embodiment, the orientation is parallel to the cell wall with, for example, about seventy percent of the layers being within thirty degrees of parallel with the cell wall. In the multilayer polymer film, sheet or tube embodiment, the orientation is parallel to major surface of the film, sheet or tube. In the pultrusion embodiment, the orientation is parallel to fiber bundle. In the compression molding embodiment. the orientation is parallel to the reinforcing fibers. In the strand foamed polymer embodiment, the layers of silicate material are partially oriented by the initial extrusion process prior to foaming and further oriented parallel to the cell wall during foaming. In the SCORIM embodiment, the alignment is parallel to the plane of the part being molded. Another important benefit of the instant invention is that its articles can be relatively large (more than one kilogram) in comparison

with articles made according to the prior art. The amount of multi-layered silicate material used in the instant invention is preferably between one and twenty weight percent.

DETAILED DESCRIPTION OF THE INVENTION

The term "multi-layered silicate material" is well known in the nanocomposite art and includes phyllosilicate clays and layered silicates. Illustrative of such materials are smectite clay minerals such as montmorillonite, nontronite, beidellite, hectorite, saponite, sauconite, and vermiculite clay minerals. This term also includes illite minerals such as ledikite and layered silicates such as magadiite and kenyaite. Preferred multi-layered silicate materials are phyllosilicates of the 2:1 type having a negative charge on the layers ranging from 0.25 to 1.5 charges per formula unit and a commensurate number of exchangeable cations in the interlayer spaces. Most preferred are smectite clay minerals such as montmorillonite, nontronite, beidellite, hectorite, saponite, sauconite, and the layered silicates magadiite, and kenyaite.

The technique used to disperse or "exfoliate" a multi-layered silicate material into a polymer is not critical in the instant invention as long as the volume percent of the one, two, three, four and five layers of silicate material so dispersed or "exfoliated" are greater than the volume percent of the more than five layers of silicate material so dispersed or "exfoliated". For example, such dispersion can be accomplished by polymerizing one or more monomers with a treated multi-layered silicate material as described in United States Patent 5,973,053, herein fully incorporated by reference or, for example, by melt blending a treated multi-layered silicate material with a polymer as described in United States Patent 5,385,776, herein fully incorporated by reference. The volume percent of single, double, three, four five and more than five layers of silicate material is determined herein by electron microscopic examination of a representative sample wherein each layer by definition herein has the same volume.

The term "structural foamed polymer" and a basic teaching regarding its process and articles will be found in the Encyclopedia of Polymer Science and Engineering, Vol. 15, 1989, p. 771-797, herein fully incorporated by reference, and is patentably different than the foams discussed in United States Patent 5,717,000. The minimum density of such foam product is often limited by the ability of the cell walls to withstand the loads which are applied during use. Conventional relatively large sized fillers like talc can be used to strengthen the cell walls. However, this can lead to premature rupture of the cell wall when the cell wall thickness approaches the size of the filler particles. This can limit how low a density of foam which can be prepared. In addition, an increase in the melt strength of the

polymer is desirable for thinner cell walls and conventional fillers do not change the melt strength substantially. The orientation of the ideally single platelet shaped nanofillers of the instant invention (and the fact that, once oriented, they project a cross section of less than a few nanometers across the thickness of the cell walls) can overcome these difficulties and lead to lower density foam products with good load bearing capabilities. The high aspect ratio of the nanofillers of the instant invention also dramatically increases the polymer's melt strength and produces compositions in which the cell wall sees the maximum reinforcement both in the melt and solidified state. Thus a lower density foam can be produced which equals the performance of higher density products.

The term "multilayer polymer film, sheet or tube" is defined in and a basic teaching regarding its process and articles will be found in the Encyclopedia of Polymer Science and Engineering, Vol. 7, 1987, p106-127 herein fully incorporated by reference and in United States Patents 3,576,707, 4,122,138, 5,443,874, 5,129,544, 5,441,781, 4,005,967, 3,739,052, 3,947,204 and 3,884,606, each of which are herein fully incorporated by reference. The multilayer coextrusion process has been used commercially to manufacture unique articles, tubes, sheets and films with 3 to 10 layers. It allows manufacture of products with layers thinner than can be made and handled as an individual ply. The layers may individually provide a specific attribute, such as barrier properties, mechanical strength, printability, or adhesion, to the overall structure. The multilayer extrusion process of the instant invention can, of course, be coupled with other processes such as solid phase forming, blow molding, stretch-blow molding, injection-blow molding and thermoforming to produce shaped articles.

The prior art multilayer coextrusion process suffers from difficulties in matching the rheology of separate layers. Mismatched rheology can lead to poor interfacial adhesion, a wavy interface and in extreme cases breakup of the interface. Thus, poor optical properties and reduced physical properties can be produced. It would also be advantageous to reduce the thickness of the individual layers in order to save on material costs. Reduction in thickness requires improved performance as well as very uniform layer structures. Conventional relatively large sized fillers such as talc can not generally be used in layers below 50 micrometers in thickness because such conventional fillers produce defects and flow instabilities. Extrusion molding processes often provide improved strength in the machine (extrusion) direction but are much weaker in the cross-direction. Mechanical processes such as molding with rotation have been developed to overcome this problem but

they require specialized additional equipment. A simple method for maintaining strength biaxially is desired.

In this embodiment of the instant invention it is found that the ease of orientation of the plate-like nanofillers provides a method to optimize the properties in both thin layers and in relatively thick layers in a multilayer coextruded article. The plate-like nanofillers of the instant invention provide added melt strength to low viscosity layers which leads to more uniform layer thickness, are small enough so that they do not disrupt even the thinnest single layer and the formation process causes a high degree of orientation of the plates thus maximizing the performance of the article produced. The small size of the plates makes them transparent so that they can be used in applications where clarity is required. The biaxial nature of the platelet reinforcement provides additional strength in the cross-direction, which is inherently weak due to the fabrication process.

The composites of this embodiment of the instant invention are particularly applicable in multilayer automotive fuel tanks, automotive gas filler tube/neck, fuel transport lines and hollow multilayer moldings such as carbonated beverage bottles. In these situations, the nanofillers of the instant invention may be incorporated into those layers responsible for the desired property, for example, barrier to gases or vapors. The nanofiller of the instant invention provides improved performance and clarity; the orientation imparted to the nanoparticles in the extrusion process maximizes the performance. In the case of fuel tanks or other large articles, the multilayer sheet may be extruded, followed by thermoforming of separate halves and welding of the halves together to make a completed structure. In the case of other large articles a multilayered tube (or "parison") can be extruded followed by blow molding or the parison into a mold of the desired shape. Sagging of the parison during extrusion and prior to blow molding can cause difficulties in reproducibly controlling the process. The high aspect ratio of the nanofiller provides substantial reinforcement of the polymer melt and thus reduces the sagging problem of a large parison. Other applications of this embodiment of the instant invention include semi-rigid containers for food and industrial materials, signage, machine and furniture side panels and appliances. The number of layers can be five to ten or more than ten layers. In addition, the article made can be more than one kilogram in weight.

Coextrusion has been used commercially to manufacture unique films, sheets and tubes consisting of from as few as 3 layers to thousands of layers where the individual layers can be less than 100 nanometers thick. The plate-like fillers are highly oriented in these films by the extrusion process which assists in the flow stability during extrusion thus

producing more intact layers. The thinner the layers, the greater the orientation and thus the greater the reinforcement. The orientation of the nanofiller also improves barrier and overall mechanical performance. Unlike conventional fillers, the thinness of the nanofillers of the instant invention allows for their presence without interfering with the optical properties of the films (or sheets or tubes).

Applications of this embodiment of the instant invention include barrier packaging for food and drugs, decorative films, nonmetallic mirrors for automotive and construction applications, transparent ultra violet or infra red reflective surfaces for windows and so forth.

The term "pultrusion" is defined in and a basic teaching regarding its process and articles will be found in the Encyclopedia of Polymer Science and Engineering, Vol. 4, 1986, p. 3-9 and 34-36 which are herein fully incorporated by reference. The practice of these processes can produce low modulus in a direction perpendicular to the fiber direction (off-axis) and poor performance due to a loss in bonding between the reinforcing fibers and the matrix material. The loss in bonding, which is attributed to a mismatch in the coefficient of thermal expansion (CLTE) between the reinforcing fibers and the matrix resin, can be particularly poor with carbon fibers.

It is an object of this embodiment of the instant invention to improve the off axis strength of the composite via nanocomposites with the high aspect ratio platelets. This improved performance can be more pronounced as the thickness of the composite is reduced due to the alignment of the nanocomposite plates via the shear induced in the pultrusion process. The reduction in the CLTE of the matrix due to the presence of the nanofiller produces a better match of CLTE's between carbon fibers and the matrix resin leading to a more intact interface. This performance is surprising because it tends not to take place with conventional filler materials such as talc or calcium carbonate. This embodiment of the instant invention can be used with thermoplastic and thermoset resins but is most often practiced with thermoset resin like epoxies, vinyl esters, vinyl ethers and urethanes. Applications include, for example, intermodal containers, building walls and panels, structural profiles for bridges, automotive body panels, auto door panels/modules and auto bumper beams.

The term "compression molding" is defined in and a basic teaching regarding its process and articles will be found in the Encyclopedia of Polymer Science and Engineering, Vol. 4, 1986, p. 79-85, 104 and 108 which are herein fully incorporated by

reference. A major problem with parts having support ribs which are made by compression molding an extruded fiber reinforced polymer pre-form can be "show through" of the support ribs when the wall thickness of the part is reduced below about 2 millimeters.

The use of a nanocomposite of the instant invention in the extruded fiber reinforced polymer pre-form reduces rib "show through" by reducing the coefficient of thermal expansion of the polymer to more closely match that of the glass fibers. The extrusion process can optimize orientation of the dispersed nanofiller of the instant invention by the use of multi-slit dies. Thus, the coefficient of linear expansion (CLTE) reduction is optimized by the extrusion process. The use of a nanocomposite of the instant invention can also produce a class A finish of the article superior to the use of conventional filler materials. This embodiment of the instant invention is especially useful to make automotive parts such as door panels, side panels, front end modules and structural instrument panels modules.

The term "strand foamed polymer" is defined in and a basic teaching regarding its process and articles will be found in United States Patents 5,527,573, 4,801,484, 5,206,082 and 4,824,720, each of which are herein fully incorporated by reference. The density of strand foams can be further reduced over standard foams using nanocomposites because the nanofiller plates of the instant invention are optimally oriented by the initial fiber extrusion process prior to foaming. Unlike conventional fillers, the small size of the nanofiller of the instant invention makes this added thinning of the cell wall possible. The added orientation of the nanofiller of the instant embodiment also improves the polymer's melt rheology leading to improved foam stability. The resulting higher dimensional stability and impact strength makes the foams prepared according to this embodiment well suited for automobile bumpers, headliners, insulation panels and interior automobile pillars.

The term "SCORIM" (Shear Controlled Orientation in Injection Molding) is defined in and a basic teaching regarding its process and articles will be found in United States Patents 4,994,220, 5,059,368, 4,925,161 and 5,160,466, each of which are herein fully incorporated by reference. The unique properties of the plate-like nanofiller of the instant invention produces a high degree of alignment across a large cross-section with minimal randomization of the particles, even during a prolonged cooling cycle. Thus larger parts are possible via SCORIM injection molding. In addition the nanofillers of the instant invention can be used for both reinforcement and rheology modification of one or more of the layers in an injection or a co-injection molded part. Applications of this embodiment of the

instant invention include refrigerator liners, automotive facia, containers and washing machine tubs.

EXAMPLE 1

Coextruded films of nanocomposite polyolefin compounds are prepared using a coextrusion line that consists of two 19 millimeter single screw extruders equipped with gear pumps (1.2 cc/revolution pumping capacity). These extruders provide two independent meltstreams into a coextrusion feedblock that provides an initial two-layer meltstream (i.e., the first composite stream). This first composite stream is subsequently passed through a series of two channel layer multipliers (similar in design to those taught by Schrenk, et al. in U.S. 5,202,074, herein fully incorporated by reference) to create a second composite stream having an increased number of layers in accordance with the following equation:

$$N = 2(2^n)$$

Where: N = Total number of layers

n = Number of layer multiplication stages

The second composite stream is subsequently passed though a 350 millimeter wide flex lip die and onto a chilled casting drum to fabricate a thin film.

The materials utilized are Engage EG8200 Brand Polyolefin Elastomer from Dupont-Dow Elastomers; PRIMACOR 3460 Brand Poly(ethylene-co-acrylic acid) from The Dow Chemical Company; PRIMACOR 1430 Brand Poly(ethylene-co-acrylic acid from The Dow Chemical Company; and Claytone HY Brand quaternary ammonium treated montmorillonite multi-layered silicate material from Southern Clay Products.

The two PRIMACOR grades and Claytone HY are precompounded using a Werner Pfleiderer ZSK30 co-rotating twin screw extruder in the follow weight ratios:

Material	wt%
PRIMACOR 1430	80
PRIMACOR 3460	16
Claytone HY	4

This compound (Compound "A", approximately 0.8 volume % multi-layered silicate) is then coextruded with the Engage (equal volumetric ratios) using the previously described process under the following conditions:

Extruder A

Material: Engage EG8200

Extruder Barrel Set temperatures (C)

Zone 1: 160

Zone 2: 185

Zone 3: 200

Gear Pump temperature: 200 C

Extruder Screw Speed: 70 RPM

Pump Speed: 35 RPM

Extruder B

Material: Compound A

Extruder Barrel Set temperatures (C)

Zone 1: 155

Zone 2: 175

Zone 3: 190

Gear Pump temperature: 190 C

Extruder Screw Speed: 70 RPM

Pump Speed: 35 RPM

Layer Multipliers temperature: 192 C

Die temperature: 220 C

The extruded films (nominal 2.5 mil thickness) were then tested for oxygen permeability and specular light transmission in accordance with ASTM test methods D3985 and D1003 respectively. The results are shown in the following table:

Sample	Composition (volume %)		Multiplication Stages	Total Number of Layers	O_2 Transmission Rate^	Percent Haze
	EG8200	Compound A				
1	50	50	2	8	500	7
2	50	50	4	32	500	7
3	50	50	4	Blend*	785	32

*Prepared by extruding a physical mixture of EG8200 and Compound A

Oxygen Transmission Rate Units: cc-mil/100 in^2-day-atm.

EXAMPLE 2

Injection molded samples of polypropylene structural foams are prepared using an Arburg 170CMD brand reciprocating screw injection molding machine equipped with an 18 mm injection cylinder, a mechanical shut-off nozzle, and a plaque mold (cavity dimensions: 65 millimeter x 65 millimeter x 6 millimeter). The mold is fed through a full width, full thickness fan gate.

The specific material formulations in parts per hundred are described in the following table:

ID	PP	3150	Claytone HY	FM1709H	
I		71.0	25.0	----	4.0
II		64.3	22.1	9.6	4.0

The materials are obtained from the following manufacturers:

H702-35 homopolymer polypropylene (PP): The Dow Chemical Company

Polybond 3150 grafted PP: Uniroyal Chemical

Claytone HY quaternary ammonium treated montmorillonite: Southern Clay Products (55 wt% inorganic multi-layered silicate material)

FM1709H Blowing Agent: Equistar

The blowing agent is azobisformamide based, and it is in the form of a concentrate in a polyolefin carrier. The PP/Polybond/Claytone HY materials employed in Formulation II were provided as a concentrate (67/23/10) prepared using a 25 mm high speed co-rotating twin screw extruder (a 30 HP Krupp Werner Pfleiderer ZSK Mega Compounder) operating under the following conditions:

Screw Speed: 1000 RPM
Extrusion Rate: 6.64 kg/hr
Torque: 35% of maximum
Barrel Set Temperatures: 150°C
Die Set Temperature: 190°C
Melt Discharge Temperature: 230°C

The respective materials for each formulation were weighed, physically mixed, and then directly fed into the feed throat of the injection molding machine. The molding conditions that are generally employed are summarized below.

Barrel Set Temp (°C)	
Zone 1:	182
Zone 2:	210
Zone 3:	221
Nozzle:	221
Plasticization Speed (m/min):	10
Back Pressure (bar):	30 (I)
	60 (II)
Shot Size (cc):	18
Fill Time (s):	0.5
Pack Pressure (bar):	25
Pack Time (s):	1
Hold Time (s):	130
Mold Temperature (°C):	19

The foam samples exhibit a density of 26 ±1 lb/ft3, which represents density reduction of 54% relative to the solid polymer. These foams are subsequently tested for compressive properties by generally following ASTM procedure D1621-94. The results are summarized in the following table.

ID	Compressive Modulus (ksi)	Yield Stress (psi)
I	11.7	448
II	12.3	536

The nanofilled material exhibited a modulus and yield strength improvement of 5% and 20% relative to the unfilled control. The nanofilled material also exhibits improved post yield properties.

EXAMPLE 3

Injection molded samples of glass fiber reinforced polypropylene compounds are prepared using an Arburg 170CMD brand reciprocating screw injection molding machine equipped with an 18 mm injection cylinder and a modified ASTM Type I tensile bar mold. The specific material formulations in parts per hundred is described in the following table:

	Homopolymer	Grafted	Claytone	Glass Fiber
ID	H702-35	PB 3150	HY	R22Y-AA
D	67	23	10	
E	60	21	9	10
F	47	16	7	30

The materials are obtained from the following manufacturers:

H702-35 homopolymer polypropylene (PP): The Dow Chemical Company

Polybond 3150: Uniroyal Chemical

Claytone HY quaternary ammonium treated multi-layered silicate: Southern Clay Products (55 wt% inorganic multi-layered silicate)

R22Y-AA: Owens Corning Fiberglas

The PP/Polybond/Claytone HY materials employed in D-F are provided as a concentrate (67/23/10) prepared using a 25 mm high speed co-rotating twin screw extruder (a 30 HP Krupp Werner Pfleiderer ZSK Mega Compounder) operating under the following conditions:

Screw Speed: 1000 RPM

Extrusion Rate: 6.64 kg/hr

Torque: 35% of maximum

Barrel Set Temperatures: 150°C

Die Set Temperature: 190°C

Melt Discharge Temperature: 230°C

The respective materials for each formulation are weighed, physically mixed, and then directly fed into the feed throat of the injection molding machine. The molding conditions that were generally employed are summarized below

Barrel Set Temp (°C)

Zone 1:	182
Zone 2:	204
Zone 3:	215
Nozzle:	215

Plasticization Speed (m/min):	5
Back Pressure (bar):	20 (200 for Samples C and F)
Shot Size (cc):	16
Fill Time (s):	11
Pack Pressure (bar):	500
Pack Time (s):	60
Mold Temperature (°C):	20

The samples are subsequently tested for flexural properties and coefficient of thermal expansion (CTE) parallel to the length axis by generally ASTM procedures D790 (Method 1 Procedure A) and E831 (-30 °C to 30 °C) respectively. The results are summarized in the following table.

Sample ID	Flexural Modulus	Yield Strain	Yield Stress	CTE
D	296.8	2.83	5230	47
E	472.5	2.87	6910	37
F	815.3	1.69	8590	27

Flexural Modulus in ksi

Yield Strain in percent

Yield Stress in psi

CTE in micro m per m-degree C

EXAMPLE 4

7.5 parts per hundred (pph) Closite 30 brand multi-layered silicate material from Southern Clay Products is blended into 5 gal of Derakane 411-350 (The Dow Chemical Company) at 7 degrees C until homogeneous. 1.5 pph of a mold release agent (Axel PS 125) and 0.3 pph of air release agent (BYK 515) is added, followed by 0.1g of a mixed catalyst containing Peracodox 16N, Trigonox 141, and Trigonox C.

A fiber package consisting of 7 layers (1 = Nexus Veil 110-039, 2 = Glass Matting (M8643, 1.5oz), 3 = Glass roving 46 strands (PPG 2026, 113 yield), 4 = Glass matting, 5 = Glass Roving, 6 = Glass Matting, 7 = Nexus Veil) is impregnated with the resin via a dip bath and pulled through a 15X3 mm flat plate pultrusion die. The curing system consists of three eight inch heating zones (240°F, 280°F, and 280°F). The final parts were 3.94 mm thick, consisted of 52 volume% resin, and 48 volume% glass with a density of 1.4-1.5g/cm^3. Test specimens are cut from the final parts and tested with the following results: Tensile strength, 72312 psi; Modulus, 3410191 psi; Strain at break, 2.3%; Elongation at break, 2.28%.

CLAIMS:

1. An improved process for making a structural foamed polymer comprising the steps of dispersing a gas-producing material into a fluid polymer at a first pressure followed by a second pressure less than the first pressure, the difference between the first pressure and the second pressure being sufficient to generate bubbles of gas in the fluid polymer, wherein the improvement comprises the step of: dispersing a multi-layered silicate material with the polymer so that the polymer has dispersed therein single layers of silicate material, double layers of silicate material, triple layers of silicate material, four layers of silicate material, five layers of silicate material and more than five layers of silicate material, the volume percent of the one, two, three, four and five layers of silicate material being greater than the volume percent of the more than five layers of silicate material.

2. An improved structural foamed polymer comprising gas cells having polymer walls, wherein the improvement comprises: the polymer having dispersed therein single layers of silicate material, double layers of silicate material, triple layers of silicate material, four layers of silicate material, five layers of silicate material and more than five layers of silicate material, the volume percent of the one, two, three, four and five layers of silicate material being greater than the volume percent of the more than five layers of silicate material.

3. An improved process for making a multilayer polymer film, sheet or tube comprising the step of coextruding layers of at least two different polymers or at least two different layers of the same polymer to form the multilayer polymer film, sheet or tube, wherein the improvement comprises the step of: dispersing a multi-layered silicate material with at least one polymer so that the at least one polymer has dispersed therein single layers of silicate material, double layers of silicate material, triple layers of silicate material, four layers of silicate material, five layers of silicate material and more than five layers of silicate material, the volume percent of the one, two, three, four and five layers of silicate material being greater than the volume percent of the more than five layers of silicate material.

4. An improved multilayer polymer film, sheet or tube comprising layers of at least two different polymers or at least two layers of the same polymer, wherein the improvement comprises: at least one polymer having dispersed therein single layers of silicate material, double layers of silicate material, triple layers of silicate material, four layers of silicate material, five layers of silicate material and more than five layers of silicate

material, the volume percent of the one, two, three, four and five layers of silicate material being greater than the volume percent of the more than five layers of silicate material.

5. The improved process of Claim 3, wherein the number of layers is ten or more.

6. The improved film, sheet or tube of Claim 4, wherein the number of layers is ten or more.

7. An improved pultrusion process comprising the steps of impregnating a reinforcing fiber bundle with a polymer and forming a structural profile, wherein the improvement comprises the step of: dispersing a multi-layered silicate material with the polymer so that the polymer has dispersed therein single layers of silicate material, double layers of silicate material, triple layers of silicate material, four layers of silicate material, five layers of silicate material and more than five layers of silicate material, the volume percent of the one, two, three, four and five layers of silicate material being greater than the volume percent of the more than five layers of silicate material.

8. An improved pultrusion structural profile comprising a reinforcing fiber bundle impregnated with a polymer, wherein the improvement comprises: the polymer having dispersed therein single layers of silicate material, double layers of silicate material, triple layers of silicate material, four layers of silicate material, five layers of silicate material and more than five layers of silicate material, the volume percent of the one, two, three, four and five layers of silicate material being greater than the volume percent of the more than five layers of silicate material.

9. An improved compression molding process comprising the step of compression molding an extruded fiber reinforced polymer pre-form; wherein the improvement comprises the step of: dispersing a multi-layered silicate material with the polymer so that the polymer has dispersed therein single layers of silicate material, double layers of silicate material, triple layers of silicate material, four layers of silicate material, five layers of silicate material and more than five layers of silicate material, the volume percent of the one, two, three, four and five layers of silicate material being greater than the volume percent of the more than five layers of silicate material.

10. An improved article, the article made by compression molding an extruded fiber reinforced polymer pre-form, wherein the improvement comprises: the polymer having dispersed therein single layers of silicate material, double layers of silicate material, triple layers of silicate material, four layers of silicate material, five layers of silicate

material and more than five layers of silicate material, the volume percent of the one, two, three, four and five layers of silicate material being greater than the volume percent of the more than five layers of silicate material.

11. An improved process for making strand foamed polymer comprising the steps of extruding a polymer through a plurality of openings to form strands and then coalescing the strands, wherein the improvement comprises the step of: dispersing a multi-layered silicate material with the polymer so that the polymer has dispersed therein single layers of silicate material, double layers of silicate material, triple layers of silicate material, four layers of silicate material, five layers of silicate material and more than five layers of silicate material, the volume percent of the one, two, three, four and five layers of silicate material being greater than the volume percent of the more than five layers of silicate material.

12. An improved strand foamed polymer article, wherein the improvement comprises: the polymer having dispersed therein single layers of silicate material, double layers of silicate material, triple layers of silicate material, four layers of silicate material, five layers of silicate material and more than five layers of silicate material, the volume percent of the one, two, three, four and five layers of silicate material being greater than the volume percent of the more than five layers of silicate material.

13. An improved SCORIM process for molding a polymer into an article comprising the step of introducing the polymer into a mold by reciprocating flow, wherein the improvement comprises the step of: dispersing a multi-layered silicate material with the polymer so that the polymer has dispersed therein single layers of silicate material, double layers of silicate material, triple layers of silicate material, four layers of silicate material, five layers of silicate material and more than five layers of silicate material, the volume percent of the one, two, three, four and five layers of silicate material being greater than the volume percent of the more than five layers of silicate.

14. An improved SCORIM molded polymer article, wherein the improvement comprises: the polymer having dispersed therein single layers of silicate material, double layers of silicate material, triple layers of silicate material, four layers of silicate material, five layers of silicate material and more than five layers of silicate material, the volume percent of the one, two, three, four and five layers of silicate material being greater than the volume percent of the more than five layers of silicate material.

15. The improved process of Claims 1, 3, 5, 7, 9, 11 and 13, further including the step of aligning the planes of the one, two, three, four and five layers of silicate material so that more than one half of the planes have the same orientation within thirty degrees as determined by electron microscopy.

16. The improved article of Claims 2, 4, 6, 8, 10, 12 and 14, wherein more than one half of the planes of the one, two, three, four and five layers of silicate material have the same orientation within thirty degrees as determined by electron microscopy.

17. The improved process of Claims 1, 3, 5, 7, 9, 11 and 13, wherein the weight percent of the multi-layered silicate material dispersed in the polymer is in the range of from one to twenty percent.

18. The improved process of Claims 1, 3, 5, 7, 9, 11 and 13, wherein the weight percent of the multi-layered silicate material dispersed in the polymer is in the range of from two to ten percent.

19. The improved article of Claims 2, 4, 6, 8, 10, 12 and 14, wherein the weight percent of the multi-layered silicate material dispersed in the polymer is in the range of from one to twenty percent.

20. The improved article of Claims 2, 4, 6, 8, 10, 12 and 14, wherein the weight percent of the multi-layered silicate material dispersed in the polymer is in the range of from two to ten percent.

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
17 August 2000 (17.08.2000)

PCT

(10) International Publication Number
WO 00/47657 A3

(51) International Patent Classification[7]: C08J 9/00

(21) International Application Number: PCT/US00/03682

(22) International Filing Date: 11 February 2000 (11.02.2000)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
60/119,816 12 February 1999 (12.02.1999) US

(71) Applicant *(for all designated States except US)*: **THE DOW CHEMICAL COMPANY** [US/US]; 2030 Dow Center, Midland, MI 48674 (US).

(72) Inventors; and

(75) Inventors/Applicants *(for US only)*: **FIBIGER, Richard, F.** [US/US]; 3870 Johns Lane, Midland, MI 48642 (US). **SUH, Kyung, W.** [US/US]; 6204 Evergreen Court, Midland, MI 48642 (US). **BARGER, Mark, A.** [US/US]; 129 Helen Street, Midland, MI 48640 (US). **SCHOMAKER, Joseph, A.** [US/US]; 2280 South Duncan Road, Midland, MI 48640 (US). **LIANG, Wenbin** [CN/US]; 6319 Aspen Cove, Sugarland, TX 77479 (US). **MACKEY, George, A.** [US/US]; 6007 Oak Hollow Court, Midland, MI 48640 (US). **TUNG, Harvey, C.** [US/US]; 684 Carriage Court, Newark, OH 43055 (US).

(74) Agent: **KORFHAGE, Glenn, H.**; The Dow Chemical Company, Intellectual Property Section, 2301 North Brazosport Boulevard, B-1211, Freeport, TX 77541-3257 (US).

(81) Designated States *(national)*: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, YU, ZA, ZW.

(84) Designated States *(regional)*: ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published:
— *With international search report.*

(88) Date of publication of the international search report: 18 January 2001

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 00/47657 A3

(54) **Title:** NANOCOMPOSITE ARTICLES AND PROCESS FOR MAKING

(57) **Abstract:** An improved process for making a structural foamed polymer, a multilayer polymer film, sheet or tube, a pultrusion polymer profile, a compression molded extruded fiber reinforced polymer pre-form, a strand foamed polymer and a SCORIM formed polymer article. The improvement includes the step of dispersing a multi-layered silicate material with the polymer so that the polymer has dispersed therein single layers of silicate material, double layers of silicate material, triple layers of silicate material, four layers of silicate material, five layers of silicate material and more than five layers of silicate material, the volume percent of the one, two, three, four and five layers of silicate material greater than the volume percent of the more then five layers of silicate material. In each of the above embodiments an important benefit of the instant invention is the orientation of the plane of the layers of silicate material. Preferably, most of the layers of silicate material have substantially the same orientation within thirty degrees of angle. Such orientation improves the properties of the product and provides a practical way to make larger products. The amount of multi-layered silicate material used is preferably between one and twenty percent.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 00/03682

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C08J9/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C08J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 717 000 A (SUH KYUNG W ET AL) 10 February 1998 (1998-02-10) cited in the application claims	1-20
A	US 5 164 460 A (OKADA AKANE ET AL) 17 November 1992 (1992-11-17) cited in the application claims	1-20

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
1 August 2000	18/08/2000

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Oudot, R

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/US 00/03682

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5717000 A	10-02-1998	AU 712100 B	28-10-1999
		AU 2132297 A	10-09-1997
		BR 9707867 A	27-07-1999
		CA 2247194 A	28-08-1997
		CN 1212001 A	24-03-1999
		CZ 9802639 A	13-01-1999
		EP 0882089 A	09-12-1998
		JP 2000505491 T	09-05-2000
		NO 983856 A	21-08-1998
		PL 328459 A	01-02-1999
		WO 9731053 A	28-08-1997
US 5164460 A	17-11-1992	JP 2872756 B	24-03-1999
		JP 4033955 A	05-02-1992
		DE 69111696 D	07-09-1995
		DE 69111696 T	25-01-1996
		EP 0459472 A	04-12-1991